Flexible Hybrid separation system for H2 recovery from NG Grids

Newsletter – Issue 3 – January 2018

Editorial

Welcome to this third HyGrid newsletter. HyGrid is a three year project targeting the development of a high performance, cost effective separation technology for the direct separation of pure hydrogen from natural gas grids. Three different technologies - membrane separation, electrochemical separation and temperature swing adsorption - will be combined in a new separation system to decrease the total cost of hydrogen recovery. The new separation & purification system will increase the value of hydrogen blended into the natural gas grid.

The present newsletter is the third release and it is presenting the progress on the project and highlighting information related to the R&D fields addressed. Hope you will find the info in this newsletter interesting. On our website www.hygrid-h2.eu you will find public presentations, all the public deliverables of the project and many other interesting news. Stay tuned!

In this Issue:

What is HyGrid?

The concept

One of the main problems for the implementation of the hydrogen based economy is the transportation from production centres to the end user both industries and population. To solve this problem, besides the in-situ production of hydrogen, the use of the existing Natural Gas network has been proposed for storing and distributing hydrogen. However, cost effective separation technologies for direct separation of hydrogen from the natural network should be developed for separating and purifying the hydrogen to match the end user requirements.

The HyGrid project proposes an integral solution for developing of an advanced high performance, cost effective separation technology for direct separation of hydrogen from natural gas networks. By using a novel membrane based hybrid technology combining three technologies integrated in a way that enhances the strengths of each of them (Figure 1): membrane separation technology is employed for removing H_2 from the "low H_2 content" (e.g. 2-10 %) followed by electrochemical hydrogen separation (EHP) optimal for the "very low H_2 content" (e.g. <2 %) and finally temperature swing adsorption (TSA) technology to purify from humidity produced in both systems upstream, pure hydrogen production (ISO 14687) will be obtained.

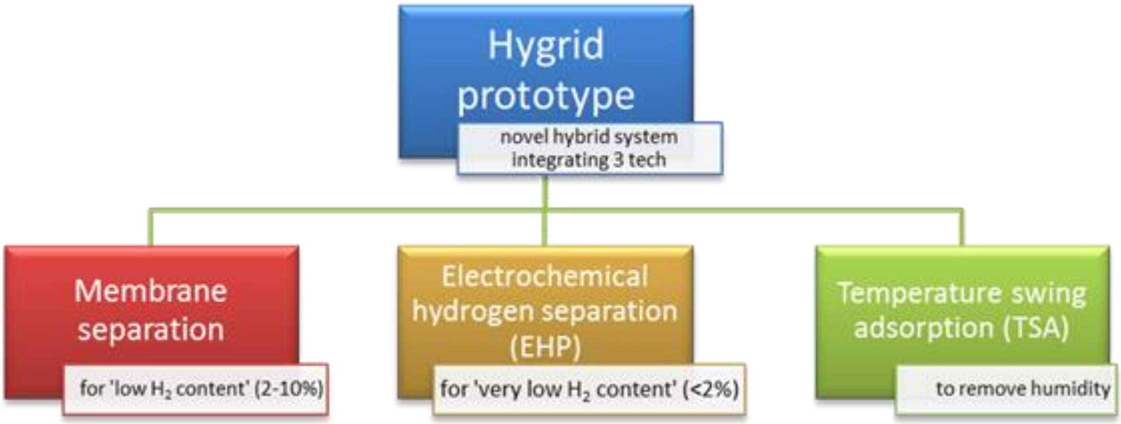


Figure 1. HyGrid concept

The new separation & purification system will increase the value of hydrogen blended into the natural gas grid, improving the economics of central hydrogen production from excess renewable energy couples with natural gas grid injection. In addition, it will reduce cost, and therefore increase the use of hydrogen from very dilute hydrogen streams in energy and transport applications. On the other side, further applications could be found in separating hydrogen from mixtures produced in chemical or biological processes, where it otherwise would be used to generate heat or even be vented.

Project objectives

The HyGrid project will develop, build and demonstrate at industrial relevant condition a novel advanced high performance, cost effective separation technology for the direct separation of pure hydrogen from natural gas grids. In particular, by combining the three different technologies (membrane separation, electrochemical separation and temperature swing adsorption) the total cost of hydrogen recovery will be decreased. The project targets a pure hydrogen separation system with power and cost of < 5 kWh/kg$_{H2}$ and < 1.5 €/kg$_{H2}$. The pilot will be designed for the separation and purification of >25 kg/day of hydrogen (ISO 14687).

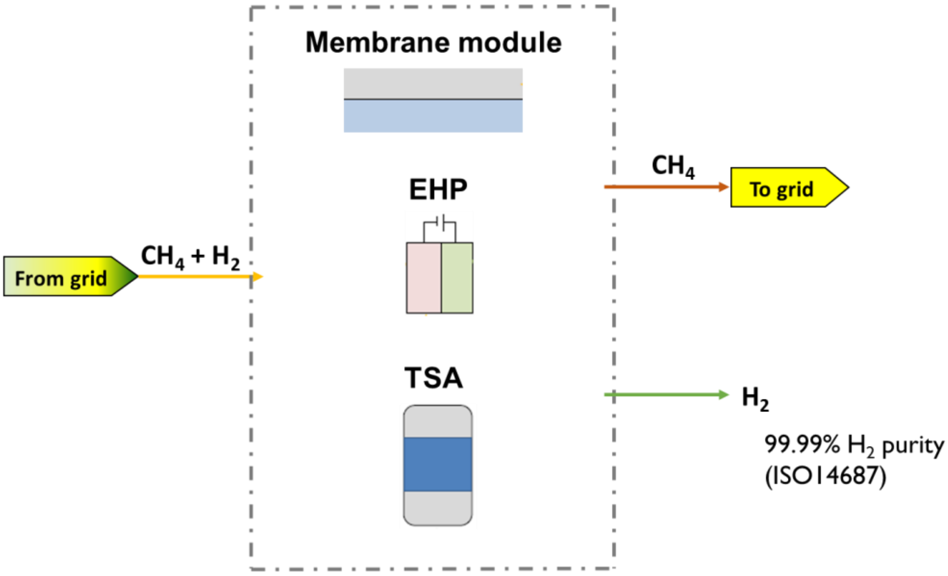


Figure 2. System schematic layout

The main objectives of the HyGrid project are:

- Design, develop, demonstrate and optimise an advanced hydrogen separation system for the production of at least 25 kg/day of hydrogen as per ISO 14687 from low (2-10%) and very low (<2%) H_2 blends in natural gas grids
- Development of stable, high performance and long durability membranes for hydrogen recovery from low (2-10%) hydrogen content streams.
- Development of more stable sealing methods for the membranes at moderate temperatures and reductive atmospheres.
- The further development of EHP for hydrogen recovery from very low (<2%) concentration streams.

- The further development of TSA for water removal from hydrogen/water streams.
- The integration of the new membranes, TSA and EHP in novel hybrid system to achieve high recoveries with low energy penalties.
- Energy analysis of the new HyGrid technology on different scenarios:
  - recovery of H_2 from low concentration streams (2% -10%) up to 99.99% H_2 purity (ISO14687) in the whole range of pressures of the NG grid.
  - Different configurations/combinations of the three separation technologies
- The validation of the novel hybrid system at prototype scale (TLR 5)
- The environmental analysis through a Life Cycle Assessment of the complete chain.
- Dissemination and exploitation of the results.

Partnership

The HyGrid consortium consists of 7 European organizations from 4 countries (Netherlands, Spain, Italy and Switzerland). HyGrid gathers the complete chain of expertise reaching the critical mass necessary to achieve the objectives of the project. The consortium brings together multidisciplinary expertise of material development (electrochemical separation, sorption and membranes), chemical and process engineering, modelling (from thermodynamics to unit operation modelling to system integration), membranes modules and reactors development, LCA and industrial study, innovation management and exploitation.

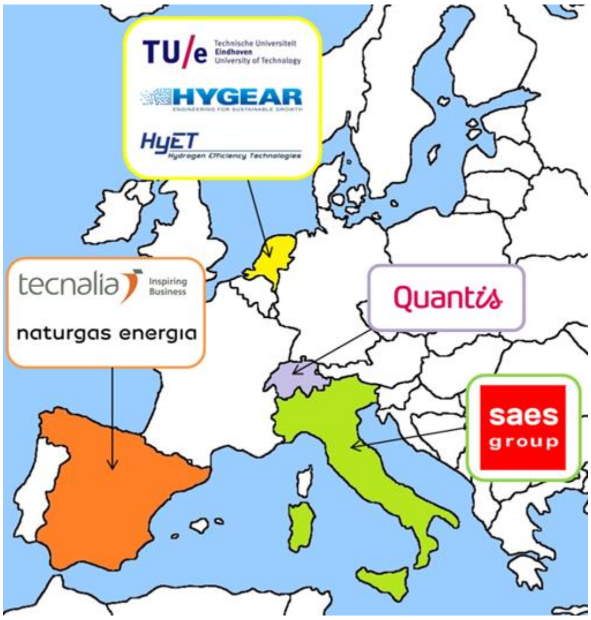


Figure 3. European partnership in HyGrid

Project structure

The HyGrid project structure is subdivided in ten work packages (see the simplified scheme below) following the focus on the development of novel (longer and more stable) membranes for H_2 separation, electrochemical separation and TSA for hydrogen separation from natural gas grids. Furthermore, the project will give a robust proof of concept, validation and assessment of the novel hybrid separation technology. The synergies between the partners are also visible in the scheme. Therefore, the work structure is based on the following work packages

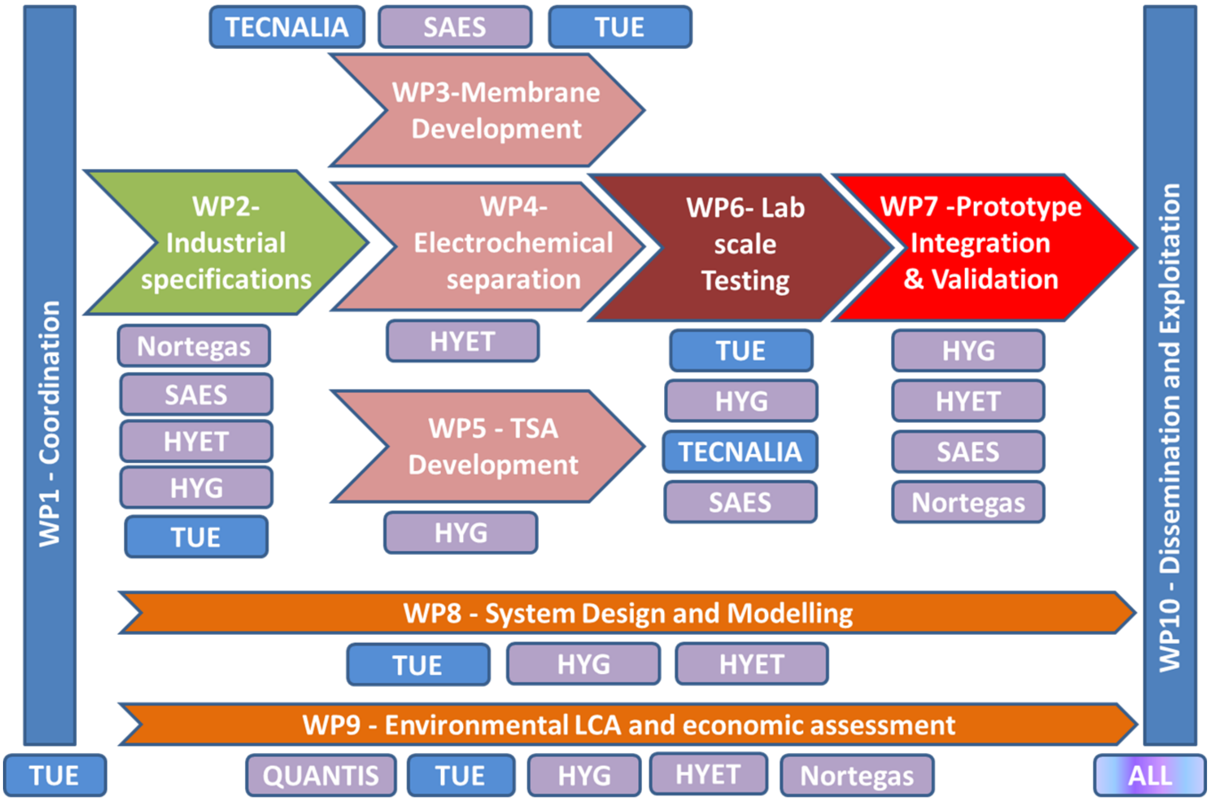


Figure 4. Work structure and synergies between partners.

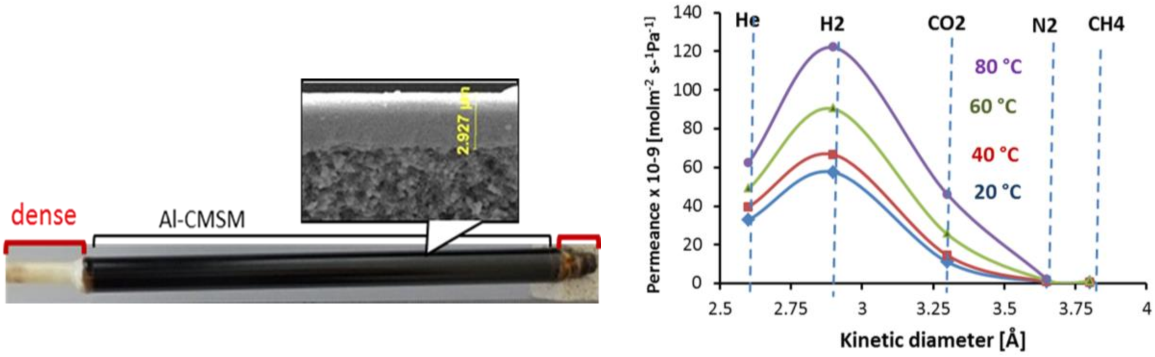
Latest news from the project

The latest news on different WP activities are now reported:

Membranes development

In HyGrid project, TECNALIA is developing supported Palladium - silver (Pd-Ag) and composite alumina carbon molecular sieves membranes (Al-CMSM). Pd based membranes have very high permeation and selectivity towards hydrogen and their best temperatures of permeation are in the range of 300 to 500 °C. In the other hand, Al-CMSM membranes have lower permeance and selectivity, but they can permeate hydrogen at low temperatures (below 100 °C) where Pd membranes can be damaged; in addition, the Al-CMSM can be prepared from cheap polymeric precursors.

Two mechanisms of permeation are involved in the permeation of gases in CMSM: a) molecular sieving that depends on the size of the gas and the size of the pores of the membranes, only the gases smaller than the pores will pass and b) adsorption diffusion in which the most adsorbable gas will preferably pass. The Al-CMSM have been prepared by the one dip-dry carbonization step on the outer surface of a porous alumina supports having 200 nm pore size (Figure 5a). The permeation of various pure gases at different pressures and temperatures were carried out at TU/e. From the gas flux at various pressures, the permeances were calculated. The permeance of the gases at various temperatures in function of the kinetic diameter is shown in Figure 5b. It can be observed that the permeance increases with the temperature; and also when the size of the gases decreases due to the molecular sieve separation mechanism. H_2, and to a lesser extent, CO_2, has a permeance higher than that expected only for the sieving mechanism; this is due to the preferable adsorption of the gases in the pores; Al-CMSM have oxygen containing functional groups that interact with H_2 and CO_2 which increases the permeation. Al-CMSMs are good candidates for the separation of H_2 in the conditions of the HyGrid project.



a) b)

Figure 5. a) Al-CMSM membrane supported on a porous alumina tube; b) gas permeances at various pressures and temperatures in function of the kinetic diameter of the gas.

a) b)

c)

Figure 6. Pd-Ag membranes supported on; a) porous alumina support where both ends are connected to Swagelok.; b) "finger type membrane" where one end is closed; c) metallic support.

The nature and the quality of the support is very important for the preparation of defect free thin Pd-based membranes. The surface of the support should have low rugosity with small pores with narrow pore size distribution; the support should be mechanically strong and offer low resistance to the passage of gases. Thin Pd-Ag membranes have been deposited by the technique of electroless plating on porous alumina and metallic supports of various diameters and configurations, some of the membranes prepared are shown in Figure 6.

Ceramic porous supports have good surface quality; however, they are difficult to be assembled in metallic reactors. SAES is developing joining techniques for having ceramic supports welded to dense ceramic tubes; a sample is shown in Figure 7.

Figure 7. Porous ceramic tube welded to a metallic dense tube.

Electrochemical hydrogen separation development

The main objective of this task is the development of a hydrogen purifier (EHP) prototype for the recovery of the hydrogen from low concentration streams ($H_2 \leq 2$ %) to be integrated in the final hybrid separation/purification prototype.

In the previous months comparative research is performed and finished on different flow field geometries and types. The flow field in an EHP is used to transport the gas to the membrane and distribute it evenly. One flow field type is chosen which has a superior performance compared to the others. With this flow field the recovery rate is higher and the performance of the EHP is more stable.

For stable purification operation also a proper water balance of the EHP cell is critical. Multiple tests have been performed in order to get the water balance right. The HyGrid energy target of 4 kWh/kg H_2 cannot be reached at the target recovery rate of 60%; it is around 4.7 kWh/kg H_2. Inversely, the recovery rate is approaching the 60% target, but still needs lowering of the internal resistance of the cell. Cell-to-cell performance uniformity also needs improvement to achieve multiple stack performance that meets specifications.

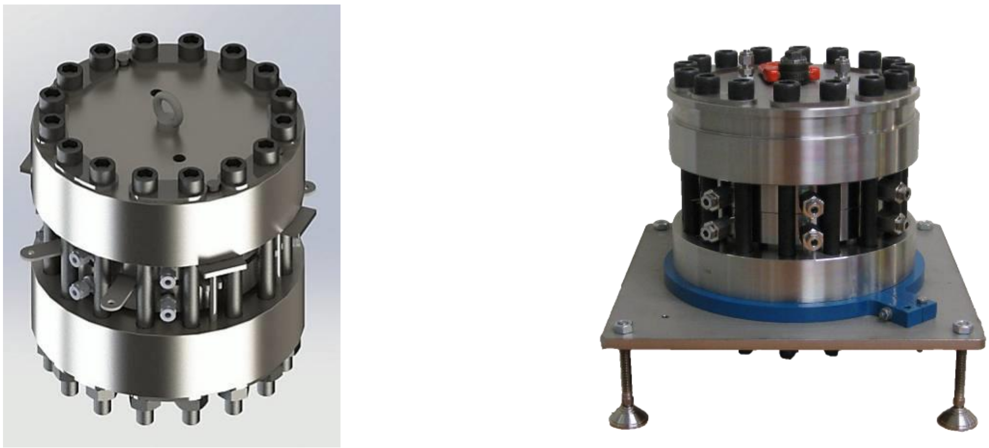


Figure 8. EHP stack platform for project HyGrid, rendered image (left) and actual platform

The majority of the tests are performed on the newly developed EHP platform, see **figure 8**. This prototype needs improvement, mainly on lowering the pressure drop of the gas flow going through the EHP platform. In the next period this optimized EHP platform will be engineered, built and tested.

In the previous periods a model of the EHP is developed on a system level to support the modeling of the complete HyGrid system. The development of a two-dimensional, multiphase, steady-state model for EHP is still ongoing, but the first results are promising and match the experimental data. This model focuses more in detail in the cell geometry of the EHP.

HyET will continue to work together with HyGear to successfully deliver the EHP module for the system.

Temperature Swing Adsorption development

In previous newsletters we reported on testing the drying capacity of different drying agents in a dedicated TSA test station in the laboratory of HyGear. The obtained data from testing confirmed the modelling results. A material selection and operational procedure definition was made based upon:

1) Product dew point reached

2) Energy required for regeneration

3) Regeneration procedure

These items were included in the build Piping and Instrumentation diagram of the TSA pilot plant to be integrated in the HyGrid prototype. Since last newsletter HyGear finished the mechanical design and assembly of the TSA pilot. Currently the TSA system is installed at the test site of HyGear. Testing the pilot TSA module is planned for the next six months.


Figure 9. TSA pilot plant under construction.

In addition the activities were started to integrate the TSA module with the membrane module by SAES and the EHP module from HyET. In the next period the design of the balance of plant for the modules will be finished and parts will be selected.

Lab scale testing

Different types of Pd-Ag membranes have been tested at different operating conditions. The types of membranes tested are conventional ceramic and metallic supported and ultra-thin ceramic supported membranes. Table 1 shows the details of the membranes tested in terms of N2 permeance at room temperature, time of plating, length, support size, H_2 permeance at 400 °C. The membrane E722 is an exception since it has been tested at 300 °C as it will explain later more in details. Figure 10 shows the ultra-thin Pd-Ag membranes E633 with 10/7 support and E737 with 14/7 support, the metallic supported membrane E681 and the membrane E722 ceramic supported brazed to a metallic tube. The membranes have been tested changing the pressure, the hydrogen molar fraction and the type of mixture in order to evaluate the influence on the hydrogen recovery factor and purity. Moreover the focus has been kept on reproducing the operating conditions of the HyGrid system in order to evaluate the hydrogen flow rate recovered.

Table 1. Description of the membranes tested.

Code	Thickness [µm]	Support size [mm]	Ideal permselectivity H_2/N_2 (1bar)@400C	Hydrogen permeance [mol/s/m^2/Pa]
E633	1.5	10/7	580	6.27E-06
E635	1.3	10/7	252	7.70E-06
E689	0.8	10/7	433	7.78E-06
E681	3-5	10/7	12056	1.99E-06
E682	3-5	10/7	1034	1.33E-06
E642	3-5	10/4	21934	2.07E-06
E582	3-5	10/7	1404	1.22E-06
E737	2-3	14/7	2428	1.49E-06
E738	2-3	14/7	731	2.2E-06
E741A	2-3	10/7	13776.5	5.8 E-06

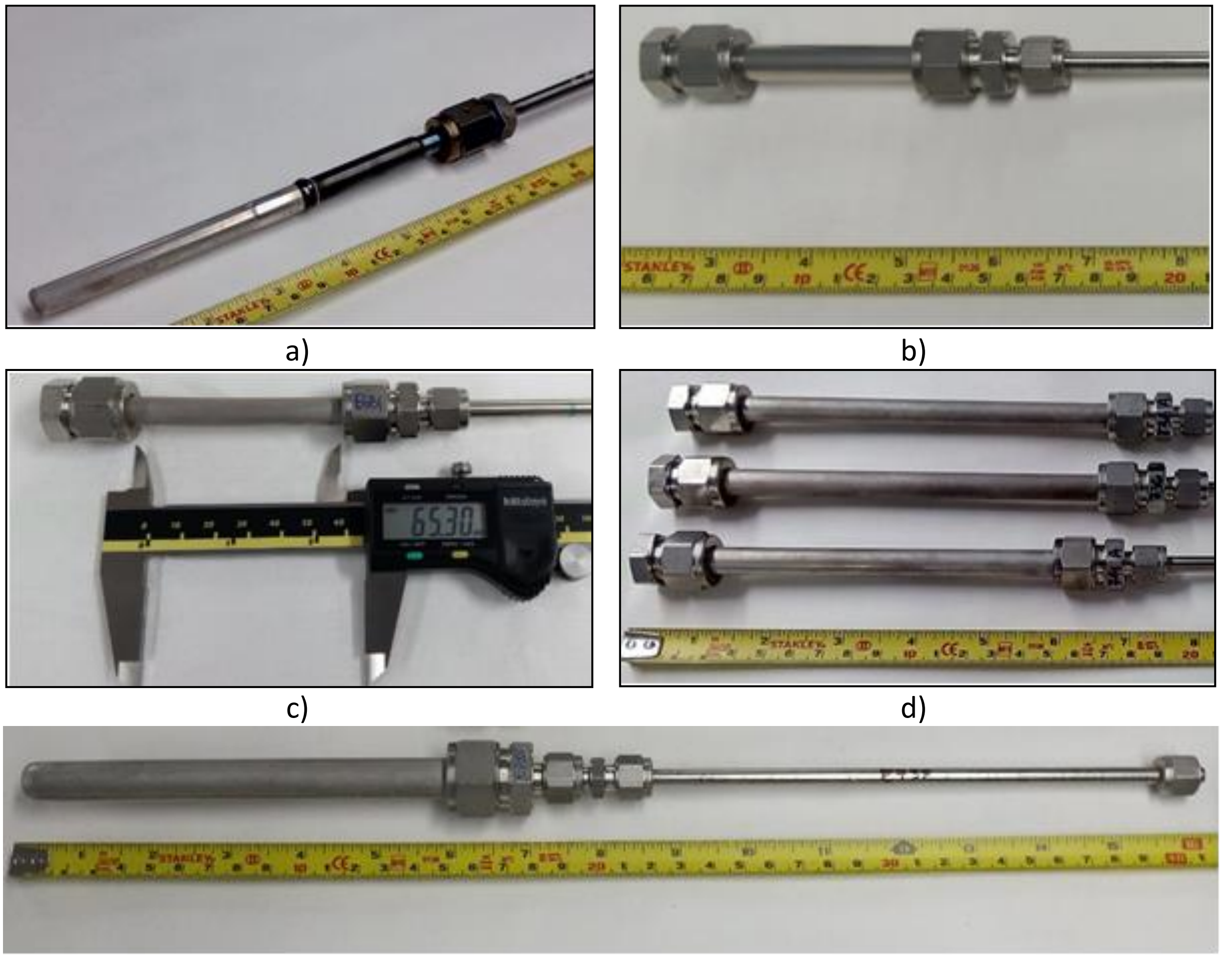

a)
b)
c)
d)

Figure 10. The membrane E722 is depicted in the top left (a), membrane E633 in the top right (b), metallic supported membrane E681 in the middle left (c) and E736a, E736b and E741a in the middle right (d) and membrane E737 in the bottom.

After pure gas tests, experiments are carried out with mixture and sweep gas. Nitrogen has been used as sweep gas. The experiments have been carried out with a mixture of methane and hydrogen. The amount of sweep gas has been changed from 0.3 to 1 l/min in order to study the influence of the sweep gas with the hydrogen permeation. In Figure 11, the results have been described. When the sweep gas is increased, the hydrogen flux is higher but there is a decrease of the recovery for higher amount of sweep gas. It could be explained by mass transfer limitation in the porous support or in the permeate side.

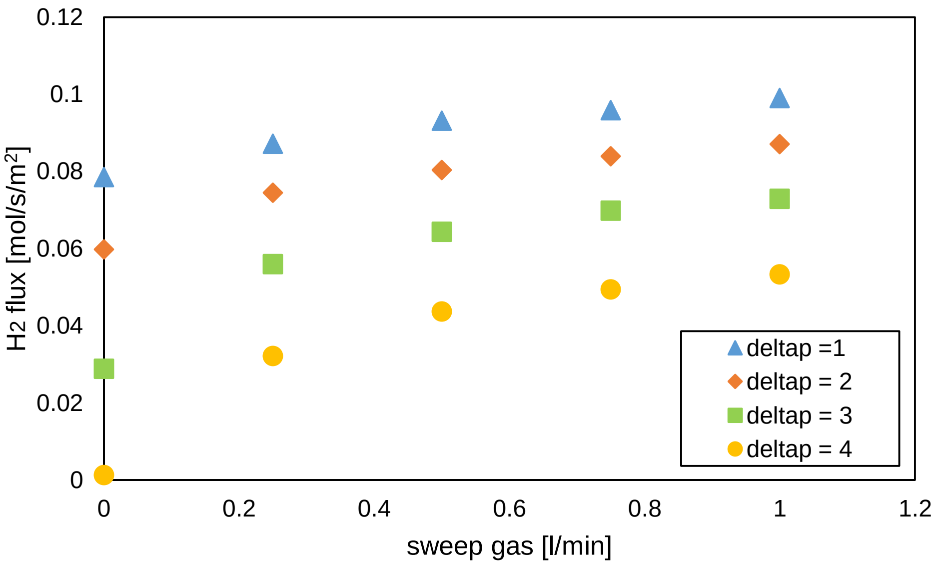


Figure 11. H_2 flux with the amount of sweep gas for different total pressure difference.

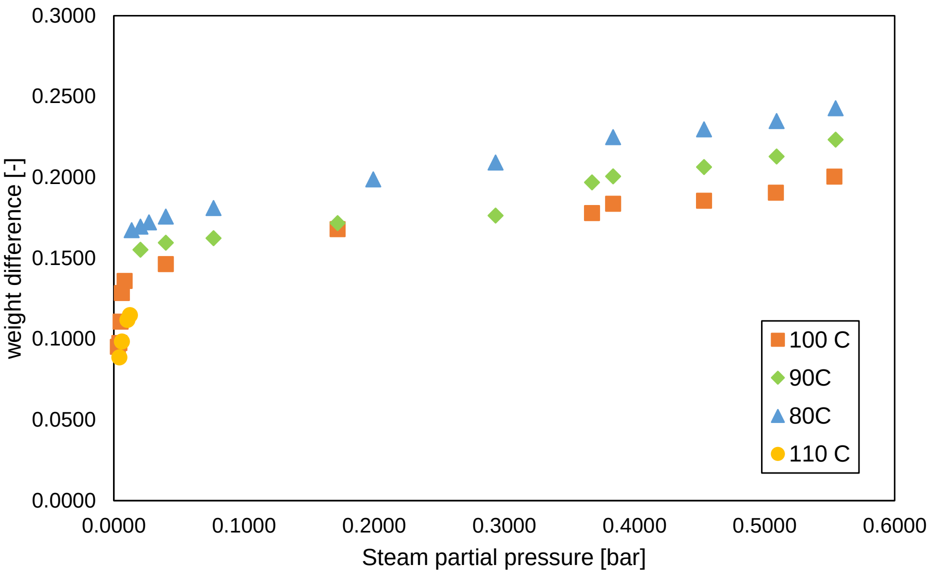


Figure 12. Isothermal adsorption changing steam pressure and temperature on silica beads.

Sorbents tests have been carried out in order to see the weight capacity for the steam. In the project, a temperature swing adsorption (TSA) is used for removing the humidity of the stream coming from the membrane. The TSA consists in sorbents columns filled with sorbents. Zeolite 4A, zeolite 13X and silica have been tested at different temperatures and steam pressure to select the sorbent with the higher weight capacity. In Figure 12 it is possible to see the results. The adsorption capacity increases at lower temperature as expected from the Langmuir law.

System modelling and simulation

A simulation of the membrane unit has been carried out in order to take into account the counter current sweep gas in the permeate side. The gas is fed in the retentate side while the sweep gas in the permeate side. Mass transfer limitation has been included in the model in order to be able to predict the real hydrogen flux once the membrane area is kept constant. In Figure 13 it is possible to see a schematic description of the membrane.

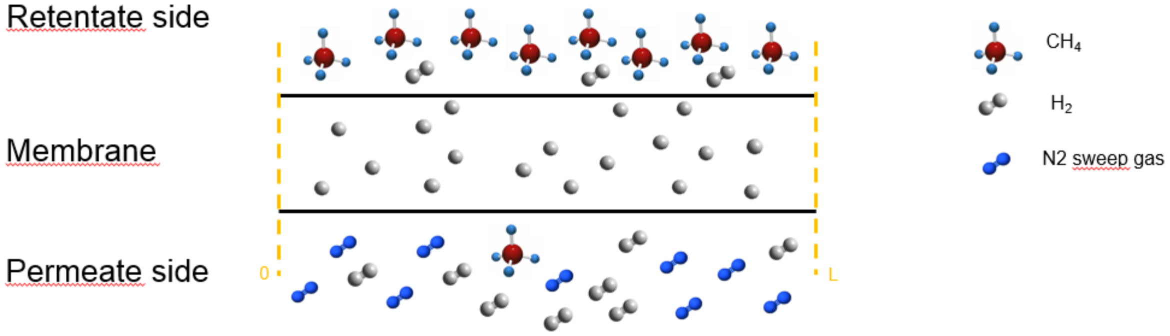


Figure 13. Schematic description of the palladium membrane

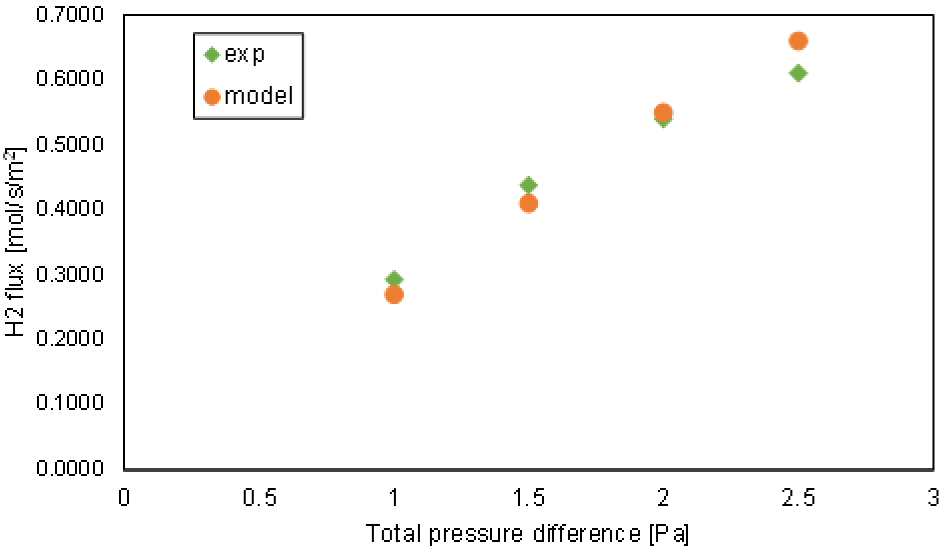


Figure 14. Schematic description of the palladium membrane

In Figure 14 a comparison between the experimental and modelled results has been depicted in order to demonstrate the validation of the model. The membrane model has been included in an aspen simulation in order to model all the different components of the project to be able to optimize the complete configuration.

Environmental and economic assessment

The environmental and economic assessment of the new hydrogen recovery systems developed within the HyGrid project will also be evaluated. The aim is not only to compare the developed technologies to current hydrogen recovery systems, but also to guide the design of the investigated technologies towards more environmentally friendly solutions. The core methodology that will be used to achieve this is life cycle assessment (LCA), a quantitative environmental assessment tool which estimates the environmental impacts of products or services looking at their entire life cycle as shown in Figure 15 below.

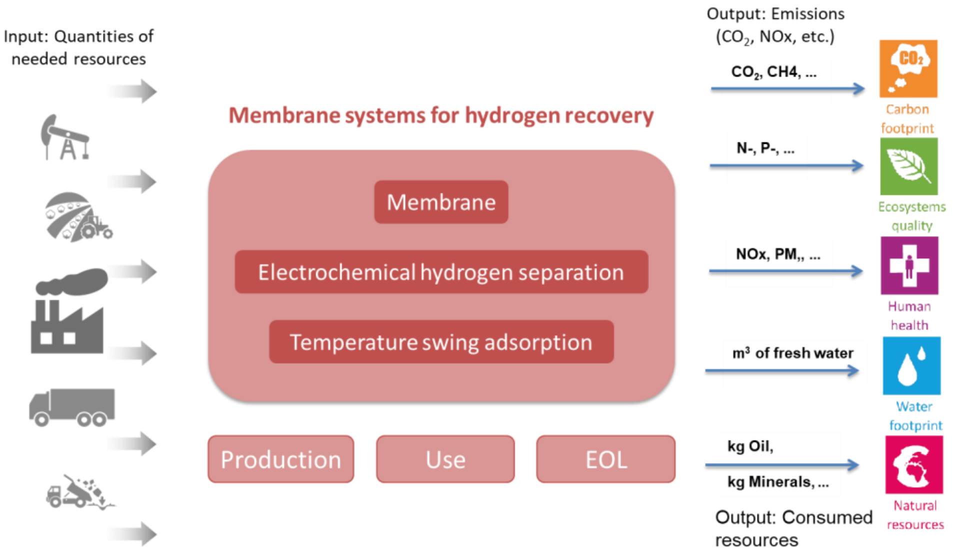


Figure 15. LCA approach

In the first 12 months, the first task of this assessment was completed which involved developing the framework for the environmental and economic assessment. In technical LCA terms, this corresponds to developing the goal and scope of the study which involves clearly defining what different systems will be analysed, what system boundaries and functional unit will be used for the study and what reference technology the HyGrid system will be compared to.

The functional unit for this study was determined to be: “the recovery of 1 kg of hydrogen with a purity of at least 99.97% from an average European natural gas grid”. Pressure swing adsorption (PSA) was identified as a suitable reference technology for the project and data were collected for this system. A key part of this project will be the data collection phase, since data from different project partners will be required to model the life cycle of the membrane systems.

The preliminary LCA results for the reference system were presented at the M18 meeting and data collection for the HyGrid system has begun. To date, the environmental impacts on all five impact categories studied (carbon footprint, water footprint, ecosystem quality, natural resources and human health) are dominated by the electricity use.

In the next 6 months, the preliminary LCA for the HyGrid system will be performed. By the end of the project, a final and detailed LCA will be performed as well as a life cycle costing (LCC) assessment. A business plan will also be developed as part of the economic assessment.

Highlights

HyGrid Workshop 2018
Exploitation Workshop on Flexible Hybrid Separation System for H2 Recovery from NG Grids
May 17th, 2018, Lainate - Italy

On 17 May 2018, a Workshop will take place in SAES Getters SpA, Viale Italia 77, 20020 Lainate (Mi), Italy. Detailed program will be available within the end of February. Please visit HyGrid website for updates (www.hygrid-h2.eu).

PROMECA Workshop 2018:
Membrane Development for Membrane Reactors
July 2018, San Sebastián - Spain

TECNALIA will host the 2nd PROMECA Workshop on Membrane Development for Membrane Reactors. The focus will be on structured catalytic membrane reactors for process intensification in hydrogen production. Selected presentation will be given on membrane development, membrane scale up, membrane stability and industrial applications of membrane reactors. Please visit PROMECA website for updates (www.promecaproject.com).

The workshop will be part of the second transfer of knowledge event of the PROMECA project, contributing to the increase of knowledge, skills, and competitiveness in the European Community of membrane reactors.

Dissemination activities, publications and presentations:

HyGrid public presentations as well as open access articles and public reports are available online in the dissemination section of the project website: www.hygrid-h2.eu.

Peer reviewed articles:

1. Margot A. Llosa Tanco, David A. Pacheco Tanaka. Recent Advances on Carbon Molecular Sieve Membranes (CMSMs) and Reactors. Processes 2016, 4, 29; doi:10.3390/pr4030029.

2. A.M. Gutierrez, J.R. Arraibi, M.A. Llosa Tanco, J. Zúñiga, J.L. Viviente, L. García Gómez. Development of carbon molecular sieve Membranes for the use of

renewable gases, biomethane and hydrogen in natural gas networks. Proceeding of the International Gas Union Research Conference 2017 (IGRC2017). Rio de Janeiro, Brazil (24-26/05/2017).

Other dissemination activities:

1. M. Nordio, F. Gallucci, M. van Sint Annaland, V. Spallina. *Flexible Hybrid separation system for Hydrogen recovery from Natural gas Grids*. Dutch membrane meeting (2016). Poster

2. Naturgas. *Una industria energéticamente sostenible.* Newspaper El Correo – Innovation section. Bilbao, Spain (1st June 2016).

3. Martijn J.J. Mulder, Peter J. Bouwman. The need for High Temperature Proton Exchange Membranes for electrochemical hydrogen purification and compression. EMEA workshop 2016. Bad Zwischenahn, Germany (27-29/06/2016). Poster.

4. A.M. Gutierrez, Flexible Hybrid separation system for H2 recovery from Natural Gas Grids (HyGrid). GERG Meeting with DG ENERGY, Brussels, Belgium (06/02/2017). Oral

5. F. Gallucci, J.L. Viviente. Flexible Hybrid separation system for H2 recovery from NG Grids. Third European Workshop on Membrane reactors: Membrane Reactors for Process Intensification (MR4PI2017). Villafranca di Verona, Italy (9-10/03/2017). Poster.

6. Marco Succi, Giorgio Macchi. Pd Supported Membrane Hydrogen Purifier: a comparison with other technologies. Third European Workshop on Membrane reactors: Membrane Reactors for Process Intensification (MR4PI2017). Villafranca di Verona, Italy (9-10/03/2017). Poster.

7. A.M. Gutierrez. Hidrógeno en redes de gas natural. Fronteras Tecnológicas en Generación de Electricidad, Energías Renovables e Hidrógeno Whorshop. Madrid, Spain (26/04/2017). Oral

8. A.M. Gutierrez, J.R. Arraibi, M.A. Llosa Tanco, J. Zúñiga, J.L. Viviente, L. García Gómez. Development of carbon molecular sieve Membranes for the use of renewable gases, biomethane and hydrogen in natural gas networks. International Gas Union Research Conference 2017 (IGRC2017). Rio de Janeiro, Brazil (24-26/05/2017). Poster.

9. M. Succi, G. Macchi, E. Fernandez, J. Melendez, J. L. Viviente, D.A Pacheco Tanaka. Advancement in Palladium Membranes Hydrogen Purification. 6th European PEFC and Electrolyser Forum. Lucerne, Switzerland (4-7/07/2017). Poster

10. D.A. Pacheco Tanaka, M.A. Llosa Tanco, J. Medrano, J. Melendez, E. Fernández, M. Nordio, F. Gallucci. Preparation and hydrogen permeation studies of ultra-thin Palladium (≈1 micrometer) and carbon membranes from mixtures containing low concentration of hydrogen (< 30%). 13th International Conference on Catalysis in Membrane Reactors (ICCMR13). Houston (Texas), USA (10-13/07/2017). Oral presentation: Key note.

11. M. Nordio, M. Van Sint Annaland, F. Gallucci, V. Spallina, M. Mulder, L. Raymakers, P. Bouwman. Electrochemical Compressor for Hydrogen Separation in a Small Scale Hybrid System. 13th International Conference on Catalysis in Membrane Reactors (ICCMR13). Houston (Texas), USA (10-13/07/2017). Oral presentation.

12. M. Nordio, J. Meléndez, E. Fernández, M. Van Sint Annaland, D.A. Pacheco Tanaka, F. Gallucci. Ultra-thin palladium-silver membranes for pure hydrogen production and separation: modelling and effect of sweep gas. 13th International Conference on Catalysis in Membrane Reactors (ICCMR13). Houston (Texas), USA (10-13/07/2017). Oral presentation.

13. M. Nordio, J. Meléndez, D.A. Pacheco Tanaka, M. Mulder, P. Bouwman, L. Raymakers, M. Van Sint Annaland, F. Gallucci. Hybrid separation system for hydrogen recovery from natural gas grids. 10th World Congress of Chemical Engineering (WCCE10). Barcelona, Spain (1-5/11/2017). Oral presentation.

Upcoming events

14-16 March 2018	European Hydrogen Energy Conference 2018 Málaga, Spain http://www.ehec.info/
20-23 May 2018	International Conference on Chemical Reaction Engineering Firenze Fiera, Florence, Italy http://www.aidic.it/iscre25/
28-29 May 2018	20th International Conference on Inorganic Membranes and Applications (ICIMA 2018), Tokyo, Japan
17-22 June 2018	22nd World Hydrogen Energy Conference (WHEC2018) Rio de Janeiro, Brazil. http://www.whec2018.com/
18-22 June 2018	15th International Conference on Inorganic Membranes, ICIM2018 Dresden, Germany https://www.icim2018.com/

25-29 June 2018	27th World Gas Conference, Washington DC, USA http://wgc2018.com/
9-13 July 2018	Euromembrane 2018 Valencia, Spain http://www.euromembrane2018.org/
6-7 August2018	20th International Conference on Inorganic Membranes (ICIM 2018), Vancouver, Canada http://waset.org/conference/2018/08/vancouver/ICIM
November 2018	FCH JU Programme Review Days 2018 Brussels, Belgium http://www.fch.europa.eu/
2-7 June 2019	8th World Hydrogen Technology Convention (WHTC 2019) Tokyo, Japan http://whtc2019.jp/
8-11 July 2019	14th International Conference on Catalysis in Membrane Reactor (ICCMR14) Eindhoven, The Netherlands

HyGrid in figures:

- *7 partners (2RES, 2 IND, 3 SME)*
- *4 countries*
- *2,847,710 € project (2,527,710 € EU funded)*
- *Start May 2016*
- *Duration: 36 months*

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More information on HyGrid (including a non-confidential presentation of the project) is available at the project website: www.hygrid-h2.eu

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Disclosure: